

# Temperature Dependence of the Optical Response of Small Sodium Clusters

Aurel Bulgac and Caio Lewenkopf

*Department of Physics, FM-15, University of Washington, Seattle, WA 98195, USA*

## Abstract

We present an analysis of the temperature dependence of the optical response of small sodium clusters in a temperature range bracketing the melting phase transition. When the temperature increases, the mean excitation energy undergoes a red shift and the plasmon is significantly broadened, in agreement with recent experimental data. We show that the single-particle levels acquire a prominent width and the HOMO-LUMO gap as well as the width of the occupied band are reduced due to large thermal cluster size and shape fluctuations. This results in a sharp increase of the static polarizability with temperature.

PACS number: 36.40.+d, 73.20.Mf, 31.20.Pv, 36.20.Kd

One of the most intriguing questions in atomic cluster physics is the understanding of the relative importance of electronic versus ionic degrees of freedom for different observables. There is clear experimental evidence for the formation of either geometric or electronic shells for sodium clusters with  $N \approx 1500 \dots 2000$  atoms [1] in the abundance spectra, depending on the cluster temperature. At the present time there is only a qualitative theoretical understanding of this experimental result [2]. Here the temperature influence on the ionic degrees of freedom, which dominate the thermodynamics, was not yet investigated and thus the question is still not satisfactorily understood. By measuring the optical response of small alkali clusters as a function of temperature the Freiburg group [3] provided further input from a slightly different perspective: The photo-depletion spectra show a strong temperature dependence of the plasmon peak and its broadening. In this work we show that these spectra can be understood quantitatively in a framework that includes electrons and ions explicitly. In qualitative terms the scenario is very intuitive: with increasing temperature the system becomes less rigid and expands. A naive estimate based on bulk values would discard this explanation since it leads to a relatively small effect. Our calculations, however, show surprisingly large expansion coefficients and fluctuations.

We discard the two customary approaches for the description of the electronic spectrum of alkali clusters as suitable for a discussion of temperature effects: The jellium model, which is very successful in describing the electronic shell effects and which leads to a qualitatively accurate picture of the electronic excitations [4], does not incorporate ions explicitly. Any shape and size dynamics has to be included by hand and driven by the bulk parameters. Much effort has also been devoted to a different approach: very sophisticated *ab initio* calculations for  $N \leq 20$  atoms [5]. This approach can provide rich information about ground state (and few isomeric) ionic configurations. The question is: How relevant is this information for understanding experimental data taken around the bulk melting temperature (for Na,  $T_m = 371$  K)?

A partial answer to this question was given in Ref. [6], where the ions were treated explicitly and the electrons only in an implicit manner. With increasing temperature, while

the cluster melts, its geometrical properties change dramatically. A cluster undergoes a significantly more pronounced thermal expansion than the bulk, and its thermal shape and size fluctuations are very large. Since the gross features of the optical response of a metallic cluster (the line shape and position) are dominated by its geometry, it was suggested in Ref. [6] that the melting can be indirectly put in evidence by studying the temperature dependence of the Mie resonance. With the exception of Refs. [7], all calculations of the electronic excitations were performed at zero temperature, which is definitely not the experimental situation. A model aiming to address temperature effects requires an explicit treatment of atoms and electrons. However, any *ab initio* scheme encompassing the coupling to the environment and the electronic excitations is a quite daunting task [8]. This invites for a somewhat simplified approach.

The approach we have chosen is based on a distance dependent Hückel/tight-binding parametrization of the LDA Hamiltonian [9], which includes effectively the 3s and 3p atomic orbitals of an isolated sodium atom. The electronic Hamiltonian reads

$$\begin{aligned} h_{ii} &= \sum_{k \neq i} \rho(R_{ik}) \\ h_{ij} &= t_{ss}(R_{ij}) - \sum_{k \neq i,j} \left[ \frac{t_{sp}(R_{ik}) t_{sp}(R_{jk})}{e_{3p} - e_{3s}} \frac{\mathbf{R}_{ik} \cdot \mathbf{R}_{jk}}{R_{ik} R_{jk}} \right] \end{aligned} \quad (1)$$

where  $R_{ij}$  is the distance between the ions  $i$  and  $j$  and  $\rho$ ,  $t_{sp}$  and  $t_{ss}$  are distance dependent fitted functions. The electronic wave functions

$$\phi_{\mu}(\mathbf{r}) = \sum_k C_{\mu}^k \varphi_{3s}(\mathbf{r} - \mathbf{R}_k) \quad (2)$$

are linear combinations of 3s atomic orbitals  $\varphi_{3s}(\mathbf{r} - \mathbf{R}_k)$  centered at sites  $\mathbf{R}_k$ , where the coefficients  $C_{\mu}^k$  are determined by the eigenvalue equation  $\sum_l h_{kl} C_{\mu}^l = \varepsilon_{\mu} C_{\mu}^k$ . The parametrization Ref. [9] leads to ground state ionic configurations in remarkable good agreement with quantum chemistry calculations [5]. The electrons are considered always in their lowest Born–Oppenheimer state and the interionic forces are given by the Hellman–Feynman force. The coupling of the ionic degrees of freedom to a thermal bath is simulated as in Ref. [6].

We discuss temperatures which are either comparable or higher than the Debye temperature for bulk sodium ( $T_D = 150$  K), where one can safely use a classical description for the ionic degrees of freedom. Presently the experiments are done at  $T > 100$  K. The relative simplicity of this electronic Hamiltonian allows us to perform rather long canonical molecular dynamics simulations of small sodium clusters (at least  $10^{-9}$  s for each temperature). Long trajectories are desirable, since the structural changes occurring in a cluster while it undergoes a phase transition are relatively slow in time. This is the main advantage of the present approach over an *ab initio* type of calculation, where a reliable description of the phase transition in a cluster is nowadays computationally prohibitive. Along each molecular dynamics trajectory, for each different spatial configuration of a cluster, we have performed RPA calculations of the optical response. In this way, at any finite temperature the cluster properties we are presenting are proper canonical averages. The RPA is implemented in the following way [10]: The polarization propagator

$$\Pi_{RPA} = \Pi_0 + \Pi_0 V \Pi_{RPA} , \quad (3)$$

is given in terms of the residual electron-electron Coulomb interaction  $V(r) = e^2/r$  and the free particle-hole propagator  $\Pi_0$

$$\Pi_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_{p,h} \phi_p(\mathbf{r}) \phi_h^*(\mathbf{r}) \frac{2(\varepsilon_p - \varepsilon_h)}{(\omega + i0^+)^2 - (\varepsilon_p - \varepsilon_h)^2} \phi_p^*(\mathbf{r}') \phi_h(\mathbf{r}') . \quad (4)$$

The response of the cluster to a weak external field  $F(\mathbf{r})$  is given by  $S = \text{Im}\langle F | \Pi_{RPA} | F \rangle / \pi$ .

We have performed calculations for a variety of clusters in the range  $4 \leq N \leq 21$ . The structural properties of neutral clusters are in good agreement with the previous analysis [6] and partially at odds with some recent results [11]. Since this Hückel parameterization was optimized for neutral clusters it should be taken cautiously when addressing charged ones. When evaporation sets in at  $T \approx 500 \cdots 600$  K our method has a further deficiency since evaporative ensembles are rather poorly described in canonical molecular dynamics. Even with these provisos, our results still reproduce nicely the main features of the experimental data [3] for single positively charged clusters.

The results for the single-particle spectra can be summarized as follows: With increasing temperature, the single particle energy levels acquire a width and the width of the occupied band decreases, see Fig. 1. The decrease in the band width is mainly due to the significant thermal expansion of the cluster. The width of the single particle energy levels has two origins: *i*) the increase with temperature of the oscillation amplitude of the ions around their equilibria and the coupling of the ionic and electronic degrees of freedom (the analogous of the bulk electron-phonon coupling); *ii*) the large thermal size and shape fluctuations of the ionic background. This last aspect is characteristic of small metal particles only and is not present in the bulk. Only the increase in the ionic oscillation amplitude with temperature, has been so far considered within a schematic random matrix approach [12]. In the insert of Fig. 1 the temperature dependence of the HOMO-LUMO gap  $\Delta\varepsilon$  distribution  $P(\Delta\varepsilon)$  is shown. We observe that for  $N \leq 20$  at temperatures  $T < 500$  K, the condition  $T \ll \Delta\varepsilon$  is always fulfilled. This insures the quality of the Born-Oppenheimer approximation. Though, the appearance of relatively small  $\Delta\varepsilon$  certainly raises serious doubts concerning the applicability of this approximation to larger clusters.

It is interesting to establish the effect of the explicit treatment of the electronic degrees of freedom on the properties of a cluster, as its temperature changes. As expected, the role of electrons is especially important in magic clusters. In particular  $\text{Na}_{20}$  is spherical at low temperatures, while in Ref. [6] it was deformed. Our simulations indicate that with increasing temperature (particularly above melting) the stabilizing role of the electronic shells is very much reduced: the studied clusters become deformed and the shape and size fluctuations are significant. This is a rather disquieting observation, since the current understanding of the electronic shell effects assumes a melted ionic background.

Experimental data [3] indicate that the optical response of sodium clusters is significantly modified as a function of temperature. At low temperatures (around 100 K) most of the oscillator strength is concentrated in a few relatively close and sharp lines, in the vicinity of the predicted Mie resonance. At higher temperatures the mean excitation energy of the response moves towards smaller excitation energies and different lines merge into a wide

structure. Both of these trends are reproduced in our calculations, see Figs. 2 and 3.

There are several possible mechanisms that can lead to the broadening of the plasmon. One can almost immediately dismiss the coupling to two particle–two hole states or to the continuum as important mechanisms, since the density of electronic  $2p$ – $2h$  configurations and the escape width for  $N \leq 20$  is insignificant in the region of the Mie resonance. The Landau fragmentation, on the other hand, certainly plays some role (and seems to be more pronounced in neutral than in charged clusters) [13]. The tight-binding model used here does not describe accurately the unperturbed single-particle excitations in the region of the Mie resonance and Landau damping plays a minor rôle here. Had we focussed the discussion only on the ionic vibrations around some equilibrium geometry corresponding to very low temperatures, our modelling would be unsatisfactory. Such plasmon broadening mechanism due to electron–phonon coupling is likely to play a significant role only for very small clusters [7,14]. Usually the plasmon line shape is linked with the shape of a cluster [4,15]: A single hump is indicative of a spherical shape, a double hump is related to an axially deformed cluster and three humps are associated with a triaxial shape [15]. The presence of several peaks cannot be uniquely linked with the cluster deformation, since departures from the simple jellium picture and the presence of shape isomers can have a similar effect. In addition there are also notable differences between the optical response of a neutral and charged clusters with the same number of electrons, see Fig. 2 and Refs. [3,16]. The measured response of a hot  $\text{Na}_{20}$ , see Ref. [16], has a double hump line shape, similar to Fig. 3, while the measured line shape for  $\text{Na}_{21}^+$  exhibits a single hump [3].

We advocate that the main mechanism responsible for the measured line width [3] is the following: Above melting temperature the ions become extremely mobile [6] and the cluster is characterized by significant shape fluctuations and not only by a static deformation. The photoexcitation is a rapid process at the ionic time scale and the response of a cluster will reflect the instantaneous geometrical arrangement of the ions. The measured spectrum is thus a properly weighted response of all allowed shapes. Therefore, the observed line shape is not an intrinsic width of the electronic excitation, but an ensemble averaged image of the

thermal shape fluctuations. Our calculations are for neutral clusters, while experiment [3] was performed on positively ionized clusters. Even though the present formalism is not well suited for charged clusters, our results suggest that both at low and high temperatures one can account completely for the line width by considering only the electron–phonon coupling and the thermodynamics of the cluster, all other effects playing a minor role only.

Even though we do not describe the details of the experimental results (exact position of peaks and overall line shape), the main temperature effects are well reproduced: the magnitude of the red shift of the average excitation energy and the magnitude of the increase of the line width with increasing temperature. This is confirmed also by the strong temperature dependence of the polarizability of these clusters, which can be independently measured. The broadening of the single–particle levels could in principle be seen in photoionization spectra. The size of the temperature effects we report on is significantly larger than one would have expected from the study of similar bulk properties. This shows once again that atomic clusters are in more respects rather unique objects.

We express our thanks for useful discussions to G.F. Bertsch, S. Bjørnholm and D. Tománek and in particular to N. Ju. We also thank F. Spiegelmann for sending us additional tight–binding parameters [9]. Financial support from the National Science Foundation and the Department of Energy is greatly appreciated.

## REFERENCES

- [1] T.P. Martin *et al.*, J. Chem. Phys. **100**, 2322 (1994); T.P. Martin *et al.*, Z. Phys. **D 19**, 25 (1991); *ibid.*, Chem. Phys. Lett. **172**, 209 (1990).
- [2] P. Stampfli and K. H. Bennemann, Z. Phys. **D 25**, 87 (1992); *ibid.*, Phys. Rev. Lett. **69**, 3471 (1992).
- [3] Th. Reiners *et al.*, Chem. Phys. Lett. **215**, 357 (1993).
- [4] W. A. de Heer, Rev. Mod. Phys. **65**, 611 (1993).
- [5] V. Bonačić-Koutecký, P. Fantucci and J. Koutecký, Chem. Rev. **91**, 1035 (1991).
- [6] A. Bulgac and D. Kusnezov, Phys. Rev. Lett. **68**, 1335 (1992); *ibid.*, Phys. Rev. B **45**, 1988 (1992); A. Bulgac and N. Ju, Phys. Rev. B **48**, 2721 (1993).
- [7] Y. Wang *et al.*, Chem. Phys. Lett. **205**, 521 (1993); R. Poteau, D. Maynau and F. Spiegelman, Chem. Phys. **175**, 289 (1993).
- [8] P. Ballone *et al.*, Europhys. Lett. **8**, 73 (1989); U. Röthlisberger and W. Andreoni, J. Chem. Phys. **94**, 8129 (1991).
- [9] R. Poteau and F. Spiegelmann, Phys. Rev. B **45**, 1878 (1992).
- [10] G.F. Bertsch, *et al.*, Phys. Rev. Lett. **67**, 2690 (1991); N. Ju, A. Bulgac and J.W. Keller, Phys. Rev. B **48**, 9071 (1993).
- [11] R. Poteau, F. Spiegelmann and P. Labastie, Z. Phys. **D 30**, 57 (1994).
- [12] V. Akulin and G. Kurizki, Phys. Lett. **A 174**, 267 (1993).
- [13] C. Yannouleas, *et al.*, Phys. Rev. Lett. **63**, 255 (1989).
- [14] G. F. Bertsch and D. Tománek, Phys. Rev. B **40**, 2749 (1989); J. Pacheco and R. A. Broglia, Phys. Rev. Lett. **62**, 1400 (1989).
- [15] J. Pedersen *et al.*, Z. Phys. **D 26**, 281 (1993).



[16] S. Pollack, C. R. C. Wang and M. M. Kappes, J. Chem. Phys. **94**, 2496 (1991).

## Figure Captions

FIG.1 Probability distribution  $P(\varepsilon_{s.p.})$  of single-particle energies in  $\text{Na}_{20}$  for  $T = 150, 350$  and  $450$  K. Insert: gap energy distribution  $P(\Delta\varepsilon)$  for the same temperatures. An increase in  $T$  corresponds to broader distribution.

FIG.2 Oscillator strength for  $\text{Na}_8$  as a function of energy  $\omega$  for  $T = 150, 350$  and  $450$  K. Insert: the same for  $\text{Na}_9^+$ ,  $T = 150$  and  $450$  K. An increase in  $T$  causes a red shift in the response.

FIG.3 Oscillator strength for  $\text{Na}_{20}$  as a function of energy  $\omega$  for  $T = 200, 300$  and  $400$  K. Insert: polarizability  $\alpha$  (normalized to one atom  $\alpha_1$  [4]) as a function of the r.m.s. radius  $r$  for the same values of  $T$ . Increasing values of  $r$  correspond to increasing  $T$ . Error bars correspond to the variance of the respective quantities due to thermal fluctuations.





